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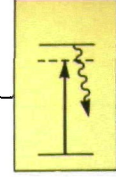

Laser spectroscopy can now pinpoint elusive rare isotopes with exceptionally high sensitivity

Detection of very rare isotopes

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AND
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THE development of modern laser spectroscopic methods has made it possible to obtain unique results in various areas of spectroscopy. Doppler-free non-linear spectroscopic techniques are capable of a spectral resolution of $R = \nu/\Delta\nu \simeq 10^{11}$, a time resolution of some 10^{-14} s, and a sensitivity that allows single atoms and molecules to be detected. One of the most complex problems that still remains to be solved is the highly selective detection of trace atoms and molecules in a real environment and particularly the detection of rare isotope atoms in the presence of a much more abundant isotope. Various approaches to this problem are under intense development.

In the world around us, there are isotopes whose concentration amounts to a negligible fraction ($<10^{-10}$) of that of the stable isotopes of the same elements. They can be detected in several ways.

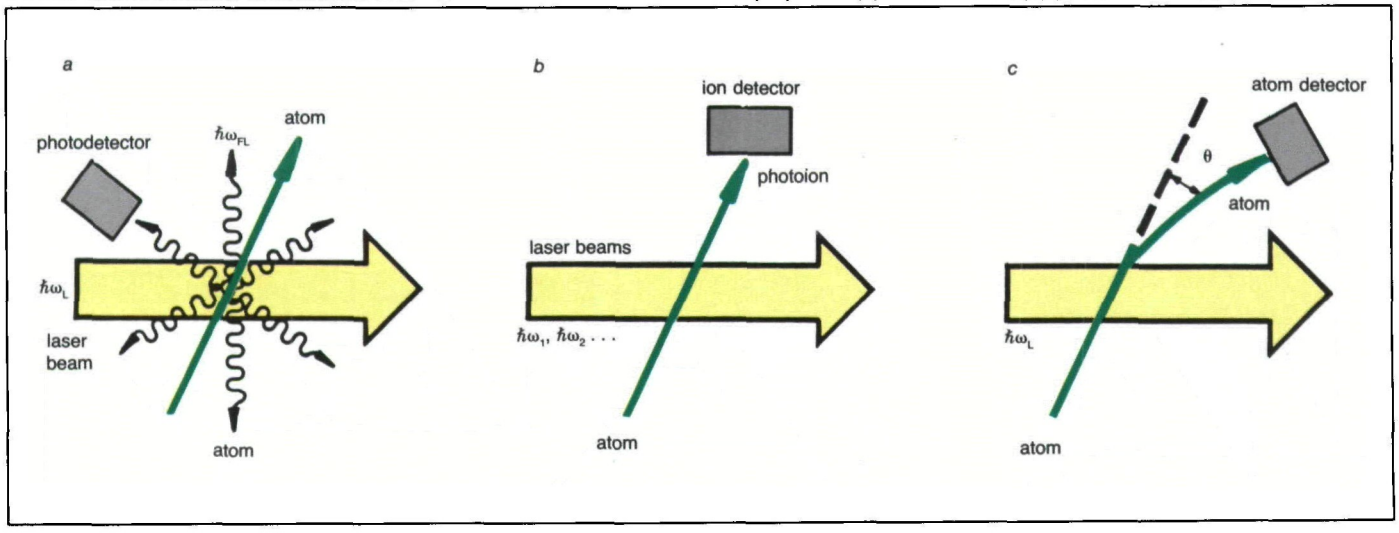
There are a fairly large number of rare isotopes of cosmic origin, particularly those formed in the upper atmosphere as a result of nuclear reactions caused by cosmic rays. They include such isotopes as ^{10}Be which results from the interaction of galactic cosmic rays with nitrogen and oxygen nuclei in the atmosphere, ^{14}C formed in the reaction between secondary neutrons and nitrogen and ^{26}Al produced as a result of splitting of an argon nucleus. These isotopes form in the upper atmosphere, precipitate, and accumulate on the Earth's surface and ocean bottom. The rate of their precipitation in the ocean can be considered to remain constant over a long period of time which exceeds their half-life.

The best known radioisotope among these is radiocarbon, ^{14}C, which is used to estimate the age of objects of organic origin. Radiocarbon, which is formed in the upper atmosphere with a concentration of $^{14}C/^{12}C = 10^{-12}$, is involved in the Earth's biochemical life cycle. When an organism dies and ceases to participate in the carbon cycle, its ^{14}C content decreases exponentially in accordance with the 5730 years' half-life of this radioisotope. To date organic archaeological objects or events of 50000 years ago, for example, it is necessary to detect ^{14}C in relative concentrations as low as 10^{-15}. By using other, longer-lived isotopes, radioisotope dating can be extended to cover millions of years in the past.

There are also a number of radioactive isotopes of technological origin (e.g. from nuclear tests and the nuclear power industry). The most abundant and dangerous artificial radioisotopes are ^{90}Sr and ^{137}Cs. These isotopes can accumulate in the living organism, ^{90}Sr concentrating in the bones, where it replaces calcium and stable strontium, and ^{137}Cs, in muscles, replacing potassium and stable caesium.

Many problems in nuclear physics also involve the determination of ultra-low concentrations of isotopes. For example, such a problem arises in the detection of solar neutrinos (the isotopes involved being ^{205}Pb, ^{81}Kr, ^{98}Tc and ^{71}Ga), in the search for exotic fractionally charged particles and in the measurement of radionuclide production cross-

1 Laser–atom interaction mechanisms which can be used for atomic detection purposes: (*a*) fluorescence; (*b*) photoionisation; (*c*) deflection



sections and long lifetimes. The table lists some rare isotopes, along with their half-lives, concentrations relative to the content of their main stable isotopes and possible applications.

At present, two universal methods exist for detecting cosmogenic isotopes in low concentrations. The first and most popular one consists of measuring the specific

Some rare isotopes

Isotope	$T_{1/2}$ (years)	Relative concentration	Application
^{10}Be	1.5×10^6	10^{-10}	dating
^{14}C	5.7×10^3	10^{-12}	dating
^{26}Al	1.4×10^5	10^{-14}	dating
^{32}Si	172	10^{-14}	ground water dating
^{36}Cl	3.0×10^5	10^{-17}	dating
^{41}Ca	8.0×10^4	10^{-14}	dating
^{81}Kr	2.1×10^5	10^{-13}	neutrino dating
^{85}Kr	10.8	10^{-11}	monitoring
^{90}Sr	28.5	10^{-10}	monitoring
^{129}I	1.57×10^7	10^{-12}	timing of geological and hydrological processes
^{137}Cs	33	—	monitoring
^{205}Pb	1.5×10^7	—	neutrino detection

radioactivity of the sample under analysis and comparing it with that of a specimen of zero age. This standard quantity for ^{14}C, for example, is well known and amounts to 15.3 beta-decay events per minute per gram of the natural mixture of carbon isotopes. To use this method requires fairly large samples (around 5 g) and a long observation time (approximately 1 day). Therefore, a major part of a very valuable sample often has to be sacrificed so that its age can be determined. Serious measures also need to be taken to ensure proper protection against background radioactivity. This method of detecting rare isotopes is disadvantageous since its operation depends on radioactive transformations of the isotopes, which occur extremely rarely. Therefore, to have a reasonable observation time (a few days), the sample must, in principle, contain a great number of the rare radioactive isotope atoms of interest.

The second method for detecting rare isotopes consists of using a tandem accelerator as a high-resolution mass spectrometer. The principal difficulty in implementing this method is the need to suppress background noise due to abundant isotopes and isotopic atoms, such as ^{14}N in the case of ^{14}C. This problem can be solved for atoms having negative ions (C^-) and lacking negative ions of isobaric atoms (N^-). The method handles much smaller samples (down to 0.1–10 mg), but the cost of the equipment required by the method is rather high.

It is clear that the shortcomings of the two generally accepted methods open up a wide field of application for laser techniques, for these are, in principle, capable of tackling the very difficult task of detecting a few rare isotopic atoms against the background of 10^{10}–10^{20} atoms of the most abundant isotope of the same atomic species.

Laser spectroscopy

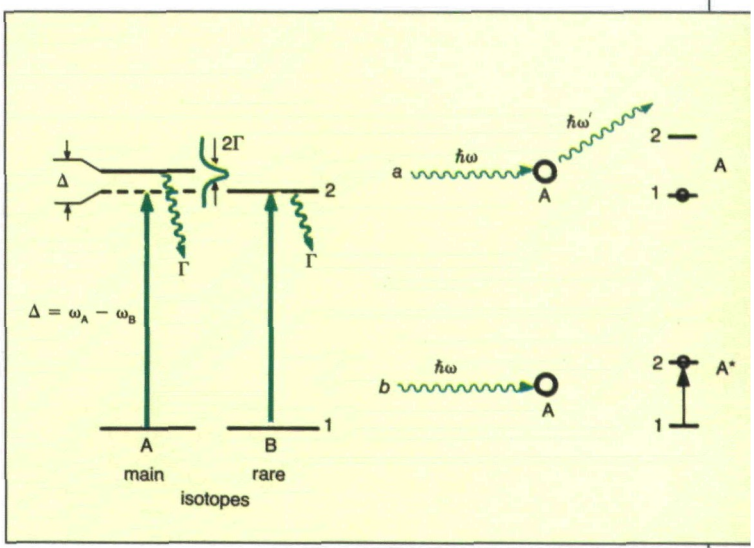
All the existing laser spectroscopy methods whose ultimate sensitivity is at the level of single atoms can, in principle, be used to effect a highly selective detection of rare isotope atoms. There are three main laser techniques that can detect single atoms, all of which take advantage of the resonant interaction of the atom with photons from the laser: (i) spontaneous re-radiation of many photons absorbed from the laser beam (figure 1*a*); (ii) photoionisation of the atom as a result of absorption of a few photons (figure 1*b*); (iii) changes of the atomic coordinate and velocity after re-radiation of a large number of photons (figure 1*c*).

The main question that relates the applicability of these methods to detecting rare isotopes is their ultimate selectivity, S, i.e. the ability to detect a small number (N_B) of the rare isotope atoms B in the presence of a much greater number (N_A) of the main isotope atoms A: $S^{-1} = N_B/N_A$. The selectivity of these techniques stems from the presence of a small isotope shift $\Delta = \omega_A - \omega_B$ of the spectral line of one or several consecutive resonant transitions of the atom from its ground state to an excited state (figure 2). The fact that the width of any spectral line is finite naturally limits the selectivity because of the overlapping of the wings of the close spectral lines of the atoms A and B, but the character of the limitation largely depends on which technique is used.

Let us consider the fluorescence technique. Resonance characteristics of fluorescent excitation lines usually have a Lorentzian shape. This means that the rate of unwanted photon scattering by the abandoned atom A when the laser frequency coincides with the centre of the spectral line of the detected rare atoms B is defined (in excitation conditions far from saturation) by the expression

$$W^A_{scat} = \sigma_0 I L(\Delta\Gamma) \simeq (1/2)(\mu_{12}E/\hbar\Delta)^2\Gamma$$

where I is the laser radiation intensity (in photons cm^{-2} s^{-1}), σ_0 the cross-section of the radiative transition 1→2 at a maximum, Γ the natural half-width or the rate of spontaneous decay of the atom into its initial ground state,



2 Limitation of the selectivity of detection of rare atoms B in the presence of abundant atoms A with a close spectral line: (*a*) fluorescence detection; (*b*) excitation detection

μ_{12} the dipole moment of the transition 1→2, E the electric field strength of the light wave and $L(x) = 1/(1 + x^2)$ the Lorentzian function. By virtue of the equation above the selectivity of the fluorescence detection of rare atoms B is limited due to the unavoidable peak fluorescence of the main isotope A to the level of

$$S_{fl} = W^B_{scat}/W^A_{scat} = (\Delta/\Gamma)^2 \; (\Delta \gg \Gamma)$$

For typical isotope shift and radiative linewidth values, $S_{fl} \simeq 10^4$–10^6, i.e. it is much lower than the required values indicated in the table.

The photoionisation technique (technique (ii)) detects excited atoms by their subsequent transition into an ionised state. Its selectivity is therefore governed by the probability of the atomic excitation and not by that of photon re-radiation. The probability of the unwanted isotope A being excited by a laser on the wing of its spectral line is

determined by the probability of absorption of two photons with the frequency $\omega = \omega_B$ and concurrent spontaneous re-radiation of a photon with the shifted frequency $\omega_{fl} = 2\omega - \omega_A = \omega + \Delta$. This probability is defined by the expression

$$W^A_{exc} \simeq (\mu_{12}E/\hbar\Delta)^4\Gamma \sim \Delta^{-4}.$$

This expression differs from the one given above for W^A_{scat}, which is the one commonly used for estimation purposes, by a stronger dependence of the excitation rate on the frequency shift Δ. The difference is substantial, but the selectivity of the method is much greater than that of the fluorescence technique but depends primarily on the type of subsequent ionisation of the excited atoms A. In the case of non-resonant simultaneous ionisation where the difference between the energy of the first absorbed photon and the atomic excitation energy, $\hbar\Delta$, can be compensated for by the second absorbed photon, selectivity is reduced to the level defined by the equation for S_{fl}. Where the atomic ionisation is a resonant process or is delayed after the excitation pulse, a higher selectivity can be achieved.

Increasing selectivity

It follows from the above simple estimates that none of the laser techniques in its simplest form can provide the very high detection selectivity that is required. However, each of the techniques can be modified so as to increase the selectivity substantially. The possible methods can be divided into two groups.

The first contains methods which are based on a *repeated* resonance interaction of the atom with laser light, wherein the atom radiates a large number of photons. In this case, there occurs what may be called a 'selectivity accumulation' caused by an effect which is possible only where a single atom re-radiates a large number of photons following its repeated resonance excitation. This effect is used in the method of 'fluorescent bursts' and in the laser deceleration and cooling of atoms.

The second group is formed from methods which use a *multistep* resonance excitation of the atom in a laser field which contains multiple frequencies, wherein use is made of isotope shifts on several consecutive resonant transitions. As a result of such a multistep resonance excitation, the selectivities S_i attained at each excitation and ionisation step can be multiplied together to increase the overall sensitivity.

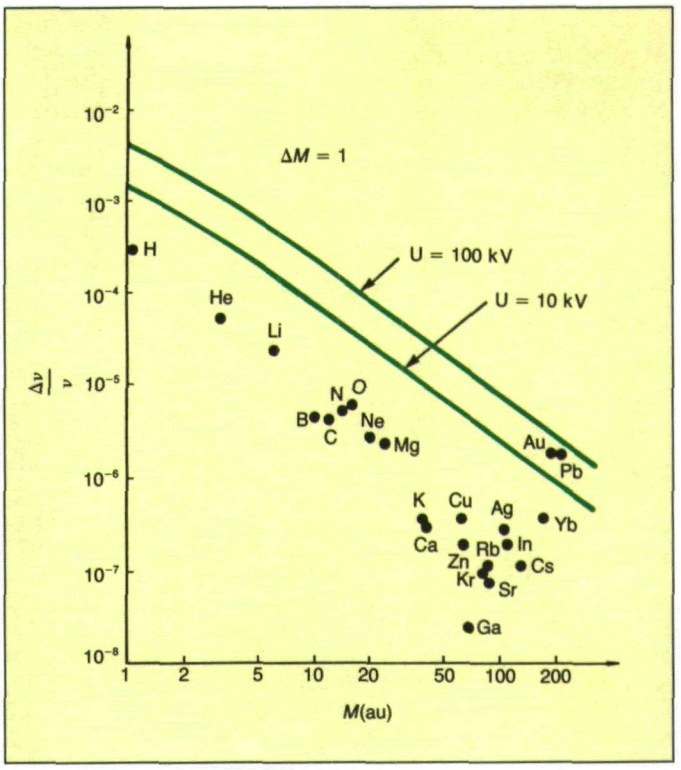
The method of 'fluorescent bursts' can be used to design a photon burst atom counter at the outlet of mass spectrometers or AMS machines so as to increase selectivity and overcome isobar interferences.

The development of high-power single-frequency CW dye lasers has allowed multistep resonance excitation to be applied to isobar-selective ionisation of atoms at the outlet of mass spectrometers.

Multistep resonance photoionisation

The idea of multiplying the isotopic selectivity, however, at each excitation step is difficult to realise for the most interesting rare isotopes (see table) because it is hard to identify a series of consecutive upward transitions with noticeable isotope shifts – such series are characteristic of the ground state only.

A universal way to overcome this difficulty and thus make the method of multistep resonance photoionisation really applicable to the detection of rare isotopes is based on collinear stepwise photoionisation of a beam of accelerated atoms. When atoms are accelerated in the form of ions under a given potential difference, U, subsequent neutralisation of the ions into atoms leads to a 'bunching' of the



3 Relative isotope shift of resonance lines of various elements (●) and kinematic isotope shift of accelerated atoms, 10 and 100 kV, as a function of atomic mass (—) for $\Delta M = 1$

longitudinal velocities. This in turn leads to a narrowing of the Doppler width of the spectral lines of the given atomic species (if viewed in a collinear fashion) as compared with the initial Doppler width, $\delta_D(0)$, at an ion source temperature of T, which is expressed as

$$\delta_D(U)/\delta_D(0) = (1/2)(kT/eU)^{1/2}.$$

At $U = 10^4$ V, the narrowing factor reaches 10^3. What is important is that in this case the atoms group into a smaller volume of the phase space and their Doppler-free spectroscopy is effected without any loss of sensitivity.

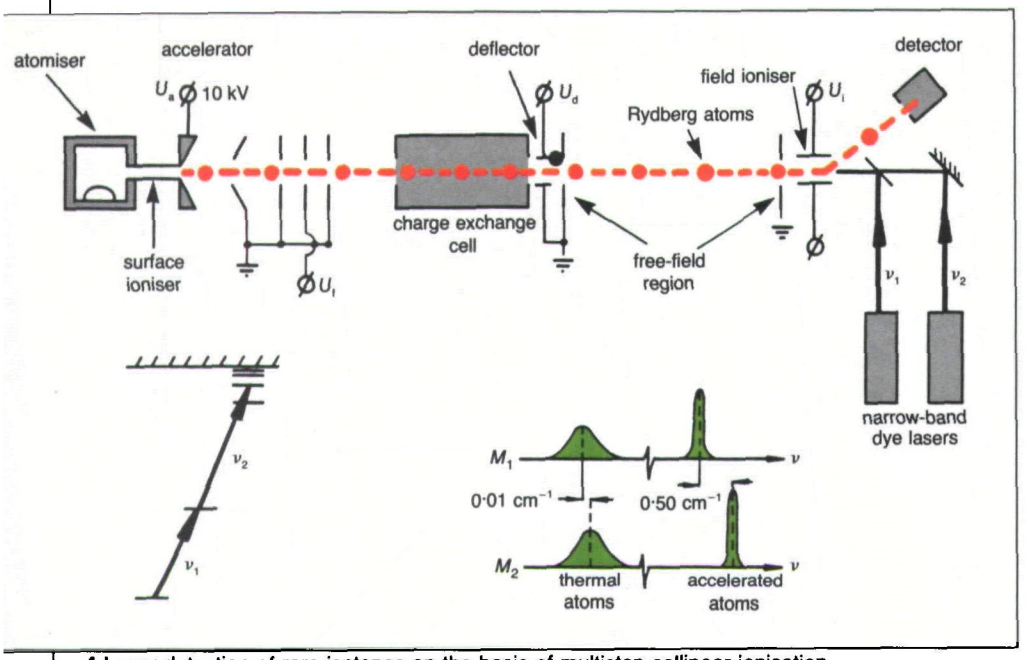
Together with the narrowing of the Doppler width, there also occurs a Doppler shift in all the spectral lines of the accelerated atoms, which depends on the mass of the ions. As a result, an artificial 'mass' shift occurs in any spectral transition of the atoms, according to the expression

$$\delta\nu_{sh}/\nu_0 = (1/c)(2eU)^{1/2}[1/(M_1)^{1/2} - 1/(M_2)^{1/2}].$$

The circles in figure 3 show the values of the natural isotope shift in resonant transitions of various elements and the artificial shift that occurs under an accelerating voltage of 10 kV and 100 kV. It can be seen that the kinematic isotope shift can increase the isotope shift by 10 to 500 times. It is particularly important that kinematic shift should be applied to the elements in the middle of the periodic table.

What is most important is that such a kinematic isotope shift occurs in any spectral transition of the atom, thus making it possible, in principle, to realise in a natural way the idea of selectivity multiplication in multistep isotope-selective excitation. Another important characteristic of this method is that it is possible to realise multistep isotope-selective excitation and ionisation of noble gas elements with a high (around 20 eV) ionisation potential by means of the dye lasers that are currently available. In that case, the atoms should have high-lying metastable states.

The general scheme of this realisation is shown in figure



4 Laser detection of rare isotopes on the basis of multistep collinear ionisation

4. A beam of fast atoms is formed by charge exchange of the ion beam with the atoms of a gas cell (alkali metal vapour, for instance). In the case of resonant charge exchange where the ionisation potential of the target atom is equal to the electron binding energy in the ground state, fast atoms are formed in the electronic ground state. To produce fast atoms which have a high ionisation potential in a metastable state, the gas cell atoms need to have an ionisation potential close to the electron binding energy of this metastable state.

Experiments on the two-step collinear excitation of accelerated potassium isotope atoms to Rydberg states, followed by ionisation in an electric field, have proved that it is possible to attain a detection selectivity of 10^5 for the isotope ^{40}K. Isotope-selective excitation in that case was performed in a single step only.

Experimental verification

To achieve the effect of multiplication of excitation selectivities in a series of excitation steps, $S = S_1 \times S_2 \times \ldots \times S_n$, was an obvious aim of the next experiment designed to improve the selectivity of detection of rare atoms. However, a great number of collisional processes were found to exert an influence on the ultimate detection selectivity. The isotope ^{3}He, with a natural concentration relative to that of the more abundant isotope ^{4}He of 1.4×10^{-6}, was chosen for the experiment.

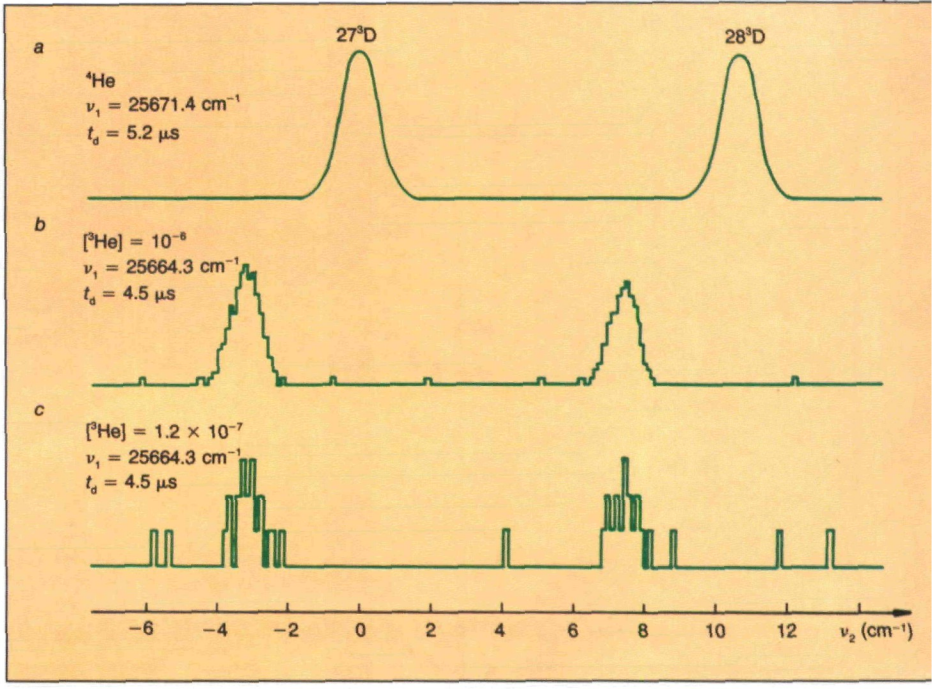
The ionisation potential of the helium atom is 24.6 eV, and so existing lasers cannot ensure its multistep ionisation from the ground state. The helium atom has two long-lived metastable states: a singlet state, 2^1S, and a triplet state, 2^3S. The charge exchange between accelerated ions and alkali metal vapour gives rise to fast neutral atoms in metastable states; potassium vapour, for example, is a good candidate for such a charge exchange. The electron binding energy of the 2^1S and 2^3S states of helium is close to the ionisation potential of potassium from its ground state $4S_{1/2}$. As a result of charge exchange, 75% of atoms are formed in the triplet metastable state 2^3S.

The isotope-selective laser excitation of accelerated helium atoms to the n^3S and n^3D Rydberg states, followed by their ionisation in an electric field, was realised through the intermediate 3^3P level. To suppress this background noise, the method can be used in conjunction with various mass spectrometry techniques. This was achieved via an additional time-of-flight separation of ^{4}He and ^{3}He, for which purpose use was made of an additional pulse intensity modulation of the continuous ion beam. This made it possible to reduce the background noise due to ^{4}He$^+$ ions by a factor of 10^4 and detect ^{3}He with a relative abundance as low as 10^{-8} (figure 5).

The technique described above for detecting ^{3}He, based on combining the collinear isotope-selective photoionisation of fast atoms with the time-of-flight separation of the isotopes, made it possible to measure the relative content of ^{3}He to levels as low as 10^{-10}. Such a determination of the isotopic composition of helium is essential to the solution of many problems in geochemistry and geophysics, cosmochemistry, oceanology and so on. The isotopic ratio [^{3}He]/[^{4}He] in various objects ranges between 10^{-4} and 10^{-10}. The method of collinear laser ionisation of fast atoms can be used to solve these problems and to detect other rare isotopes also.

Let us now consider the possibility of detecting ^{81,85}Kr isotopes by means of the laser collinear ionisation of a fast atomic beam. As can be seen from the table, these isotopes need to be detected with a selectivity of 10^{10}–10^{12}. So high a selectivity can be attained by using the kinematic isotope

5 Ion signal as a function of the second-step laser frequency ν_2: (*a*) the first-step laser frequency $\nu_1 = 25671.4$ cm^{-1} in resonance with the isotope ^{4}He; (*b*) and (*c*) the first-step laser frequency $\nu_1 = 25664.3$ cm^{-1} in resonance with the isotope ^{3}He; relative concentration of ^{3}He is (*b*) 10^{-8} and (*c*) 10^{-7}



shift concept in a two-step excitation with a narrow-band laser. However, the experiments on the He isotope detection show that the excitation and ionisation of the fast beam atoms by collision with the residual gas molecules are a considerable limitation to selectivity. To solve this problem, it is necessary either to improve the vacuum (down to 10^{-10} Torr) in the excitation and ionisation regions or to use additional mass selection. The time-of-flight isotope separation by atomic beam modulation cannot be used for such heavy elements as Kr. But collinear ionisation can rather conveniently be combined with pre-separation in a mass separator. For this purpose, at the outlet of the mass separator, the ions of the isotope to be detected separately from the ions of the abundant isotope, are directed into a charge exchange cell where they are transformed to atoms in metastable states. If the attenuation of the line wing of the abundant isotope on the mass of the isotope to be detected is 10^4, the spectral selectivity needs to be 10^6–10^8 to detect these isotopes.

The Kr atom has six stable isotopes in the following proportions: ^{86}Kr (17.3%); ^{84}Kr (57%); ^{83}Kr (11.5%); ^{82}Kr (11.6%); ^{80}Kr (2.25%) and ^{78}Kr (0.35%). The ionisation potential is 14 eV. As in the case of He, the high-lying metastable states $1S_3$ and $1S_5$ can be used as the starting states for multistep laser ionisation, since alkali metals, such as K, Rb, and Cs, have their ionisation potential close to the electron binding energy of Kr in the $1S_5$ state. There are effective transitions in Kr that can be stimulated with dye lasers pumped by a Cu-vapour laser.

The nuclear spin of all the stable Kr isotopes, except ^{83}Kr, is zero. The spectra of the rare isotopes ^{81}Kr ($I = 7/2$) and ^{85}Kr ($I = 9/2$) and the stable isotope ^{83}Kr ($I = 9/2$) are characterised by a hyperfine structure. The magnitude of the natural isotope shift is about 50 MHz per atomic mass unit, which is much smaller than that of hyperfine splitting. The hyperfine splitting constants for the above transitions are known only for the isotopes ^{83}Kr and ^{85}Kr. After acceleration to 10 keV, the absorption spectra of the isotopes become fully separated. The isotope shift of the most efficient component of ^{85}Kr is 1.9 GHz relative to ^{86}Kr, 3.4 GHz relative to ^{83}Kr, and 45.2 GHz relative to ^{84}Kr. The radiative absorption linewidth is 6.12 MHz and the laser excitation selectivity will be 3.8×10^5. The selectivity attained at the second excitation step may be no worse. Thus, isotope-selective excitation allows one to achieve a selectivity no worse than 1.5×10^{11}.

Further reading

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